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# Characterization of biomasses in the southern Italy regions for their use in thermal processes

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## HIGHLIGHTS

- Use of bioenergy sources as an alternative to fossil.
- Physical–chemical properties for an advanced use of the sustainable resource.
- Composition of biomass for the use of this fuel for energy purposes.
- Characterization of different types of biomass found in the regions of the southern Italy.

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## ABSTRACT

The attention regarding bioenergy sources, such as biomass, as an alternative to fossil fuels has increased tremendously over the past few years consequently to the problems related to global warming.

For the using of biomass as fuel is very important the basic knowledge of its physical–chemical properties for the using of the sustainable resource.

The identification of biomasses in terms of both quantification and characterization of the chemical composition of biomass is a fundamental step for the use of this fuel for energy purposes. There are many differences between the various types of biomass; firstly, the moisture, the chemical composition and in particular that of the ashes, and the content of inorganic substances.

The elements mainly present in biomass, in decreasing order of abundance are: carbon, oxygen, hydrogen, nitrogen, calcium, potassium, silicon, magnesium, aluminum, sulfur, iron, potassium, chloride, sodium and manganese. In addition, compared to coal, the chemical composition of biomass is significantly different, in particular the biomasses are highly enriched in hydrogen, manganese, potassium, phosphorus, chlorine, calcium, sodium and magnesium, as well as in terms of moisture and volatile substances compared to coal, while result with a lower ash content, iron, carbon, nitrogen, sulfur, and silicon.

The purpose of this work is the quantification and characterization of different types of biomass found in the regions of the southern Italy with similar soil and same climatic conditions, at the end of their use in mixtures in an optical of build several ultrashort bioenergetical chains. Experimental results have shown that the heavy metal content is significantly lower in the fly ash than the bottom ash, and therefore, their mixture may be used as a soil improver to maintain the cycle of nutrients in soils.

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## 1. Introduction

Power and thermal energy production from biomass gasification can represents a good solution in particular for rural areas where the retrieval of biomass is not a problem and at the same time electricity and thermal energy are required, such as near the forested areas at the end to preserve it by fires [1].

The understanding of the ashes thermal behavior, properties and their environmental impact in the long term can represent a high risk for the development of a scenario for the power generation, heat and liquid and gaseous biofuels from biomass that need to be evaluated and studied. Using ash as a byproduct of thermochemical processes is limited by the presence of heavy metals and others inorganic compounds formed as a result of the cracking reactions. The most interesting materials considered for the paper are substantially represented by solid biofuels derived from various manufacturing processes, in order to have a range of characterized matrices available that are present in the same production

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**Nomenclature**

| | |
|---|---|
| UNI EN | National Agency of unification |
| CEN | European Committee for Standardization |
| ISO | International Organization for Standardization |
| DIN | Deutsches Institut für Normung |
| ASTM | International Standards Worldwide |
| HHV | Higher heating value |
| LHV | Lower heating value |
| AI | Alcaline Index |
| $R_{a/b}$ | acid–base ratio |
| $m$ (g) | material weight expressed in gram (g) |
| $Q_i$ (J) | is the sum of heating value non product from the combustion (i.e. metal wire, capsules and other materials) |
| $\Delta t$ (°C) | temperature increase measured in the system calorimetric |
| $F$ (% p/p) | condensed water in the bomb calorimeter, expressed as % by weight of the sample determined by weighing or calculated on the basis of the reaction stoichiometry of the hydrogen contained in the sample and moisture |
| 24.41 (J/g) | factor for the latent heat of evaporation of water |
| $C$ (J/°C) | thermal capacity of the system. Is determined by burning in the same system a known amount of a reference substance of which is already known to the HHV |
| HPLC | High Performance Ionic Chromatography |

areas. In several cases the combination of some metals with porous char has a positive effect respect to the syngas cleaning [2].

The main biomass examined are:

- Food residues.
- Forestry residues.
- Residues from the manufacture of wood.

In particular, samples that fall under neither type, identified and partly collected for characterization are:

- olive residues;
- pruning:
  - olive;
  - grapevine;
  - other overall;
- almond shells;
- apricot kernels;
- Residual forest from maintenance woods:
  - cerris;
  - oak;
- sawmill waste;
- wheat straw;
- corn residue

## 2. Experimental work

### 2.1. Feedstock characterization

For the classification of biofuels taken into account, reference was made to the UNI EN 14961 norms “Specifications and Classes Solid Biofuels, General Classification.”

The classification is based on the nature and origin of biofuels useful to evaluate the material for applications in energy use. The analysis were carried out according to the UNI EN issued by CEN TC 335 to supplement and replace other standards (ISO, ASTM, TAPPI, etc.). In particular:

- Dry matter percentage (DM%).
- Content ash content.
- Determination of macro-elements: Al, Ca, Fe, K, Mg, Na, P, Si.
- Determination of trace elements Cd, Cr, Ti, Cu, Ni, Pb, Zn.
- Lower and Higher Calorific Value (q v, net).
- Volatile Substance% (volatiles).
- Fixed Carbon% (Fix C).
- Elemental analysis (C, H, N and O).
- Content of Cl, S.
- Percentage of extractives, hemicellulose, cellulose and lignin.

These data are important in the realization of mass and energy balances and in the preliminary estimate of any possible inorganic contaminants, such as HCl, $H_2S$, $NH_3$ of the raw-gas, fly ash and for the management of the ashes of the queue obtained as a byproduct of the thermochemical processes.

At this stage, parameters such as bulk density and particle size distribution have not been determined; these measures, given their peculiarities, will be carried out on batches of materials intended for use in implantation.

The possible use of a mix of biomass must be properly assessed, taking into account the ash content of each fraction and its composition since they can create conditions in which there is formation of ash that melting at lower temperatures resulting in softening and melting induced problems.

Given, however, that the ash content, and their composition depends only on the type of biomass, especially from the areas and the land in which the plant is cultivated it follows that also the thermal behavior of the same is affected; the determination of the temperature range ash melting will be determined on lots of biocombustible actually used in the plant which will be built under the project.

Characterization are listed below:

Table 1 shows the methods that are used for biomass characterization. For each one samples and their preparation was performed in the laboratory according the UNI EN 14780 with manual division technique and then reduced with a knife mill with a sieve less than 1 mm.

## 3. Methodology

### 3.1. Higher heating value

Higher heating value is the main parameter for the characterization of biomaterials for the conversion for the energy recovery.

The measure was carried out with calorimetric method in adiabatic condition with an IKA C 4000 Mahler’s bomb.

The international methodology used refers to standards ISO 1928, DIN 51900, ASTM 240 D. This methodology requires the measure of a fixed quantity of material that is burn in oxygen atmosphere at 30 bar. Pure oxygen is in excess respect to the stoichiometric quantity required for the combustion at the end to obtain the complete combustion of the solid combustible. The heat developed by the combustion is transferred to the water bath of the calorimeter vessel thereby increasing its temperature. To the increase of temperature is possible to evaluate the higher heating value and lower heating value, HHV and LHV respectively, as you can see in the equations below:

$$\mathrm{HHV}\left(\frac{J}{g}\right) = \frac{(C \times \Delta t) - Q_i}{m} \tag{1}$$

**Table 1**
Methods used for biomass characterization.

| Determination | Analytical methodology |
|---|---|
| Sampling | CEN/TS 14779 |
| Reduction and preparation | CEN/TS 14780 |
| Umidity (UM %) | EN 14774-1 |
| Ashes content | EN14775 |
| Macroelements: Na, Ca, Mg, K, Fe, Al, Si, P | EN 15290 |
| Microelements: Cd, Pb, Cr, Ti, Cu, Zn, Ni | EN 15297 |
| Higher Heating Value (HHV) | UNI EN 14918, ISO 1928, DIN 51900, ASTM 240 D |
| Lower Heating Value (LHV) | UNI EN 14918, ISO 1928, DIN 51900, ASTM 240 D |
| Volatile Matter% (VM%), | EN 15148 Modif. ASTM 3175 |
| Fixed Carbon % (FC%) | Modif. ASTM 3175 |
| Elementary analysis: C, H, N, O | EN 15104 with Elementar analyzer 2400 CHNS P.E. |
| Cl, S | EN 15289 |
| Extractive | Estazione in soxlet CPPA G13 |
| Lignin | TAPPI T13 m-54, TAPPI 250, Met. Klason |
| Carbohydrates | Met. Klason TAPPI T13 m-54, TAPPI 250, HPIC |

$$\mathrm{LHV}\left(\frac{J}{g}\right) = \mathrm{HHV} - (24.41 \times F) \tag{2}$$

where:

| | |
|---|---|
| $m$ (g) | Material weight expressed in gram(g) |
| $Q_i$ (J) | Is the sum of heating value non product from the combustion (i.e. metal wire, capsules and other materials) |
| $\Delta t$ (°C) | Temperature increase measured in the system calorimetric |
| $F$ (% p/p) | Condensed water in the bomb calorimeter, expressed as% by weight of the sample determined by weighing or calculated on the basis of the reaction stoichiometry of the hydrogen contained in the sample and moisture. |
| 24.41 (J/g) | Factor for the latent heat of evaporation of water |
| $C$ (J/°C) | Thermal capacity of the system. Is determined by burning in the same system a known amount of a reference substance of which is already known to the HHV (i.e. benzoic acid $C_6H_5COOH$). Under these conditions for C is calculated by: |

$$C\left(\frac{\mathrm{J}}{^{\circ}\mathrm{C}}\right) = \frac{(\mathrm{HHV} \times m)_{Benzoicacid} + Q_i}{\Delta t} \tag{3}$$

Fig. 1 shows both the higher and lower heating values obtained from the experimental tests on the biomasses evaluated in this work.

Experimental results offer the possibility to see that all the biomasses of this study have an higher heating value in the range of 10–18 MJ/kg.

### 3.2. Organic components of biomasses: structural and non-structural

#### 3.2.1. Structural organic components: cellulose, hemicellulose and lignin

Biomass can be considered as a complex mixture of organic structural components, composed by cellulose, hemicellulose and lignin, and others organic components such as non-structural. Cellulose and hemicellulose are the structural components of biomass, consisting of polysaccharides, glucans and glucosani for cellulose, while xilani, poliosis and pentoses for hemicellulose; lignin vice versa is a polymer of phenolic nature that has a very complex three-dimensional structure. The long polymers of cellulose fibers gives at the plants their resistance, while lignin has function of glue to hold together the same. The hemicellulose has the fundamental role of keeping associated with cellulose and lignin.

Cellulose is insoluble in water and represents the support structure of all the biomass; it is a very stable structure because has the rings with six carbon atoms, absence of double bonds and a system of hydrogen bridges between polymers, while hemicellulose is soluble in dilute alkaline solutions and is composed by different branched structures in dependence on which type of biomass, woody or herbaceous.

Lignin also performs the task of reducing the water permeability intervening in all the processes of minerals exchange, nutrients and metabolic Moreover, if the cellulose provides the mechanical strength characteristic of the wood, lignin acts as filler and glue between the plant cells, providing compressive resistance and shocks.

### 3.3. Analytical methods for characterization of cellulose, hemicellulose, lignin and extractives

The analyzes were carried out by means of solvent extraction with a mixture of ethanol – toluene with 1–2 ratio in Soxhlet apparatus for 8 h with the dry sample at 105 °C. At the end of the extraction were removed catechols, tannins, oils, waxes, resins and fats. The average value of two extractions, is expressed as percentage by weight of the total extractives compared to the sample.

The determination of lignin takes place by treating the material, already subjected to solvent extraction, first of all with concentrated sulfuric acid (72% w/w) and then maintaining the boiling point of the diluted solution (3%) at the end to complete the hydrolysis of the chains of carbohydrates to monomeric sugars. The insoluble residue consists of lignin (Klason lignin) and its weight is determined on a dry basis at 105 °C, while a lot of lignin remains in solution and is determined by UV spectrophotometry.

The acidic solution mentioned above is analyzed by HPLC (High Performance Ionic Chromatography) to determine the concentration of sugars.

The reference methods used for this determination are TAPPI T13 m-54, TAPPI 250; CPPA G13; LAP 002 NREL.

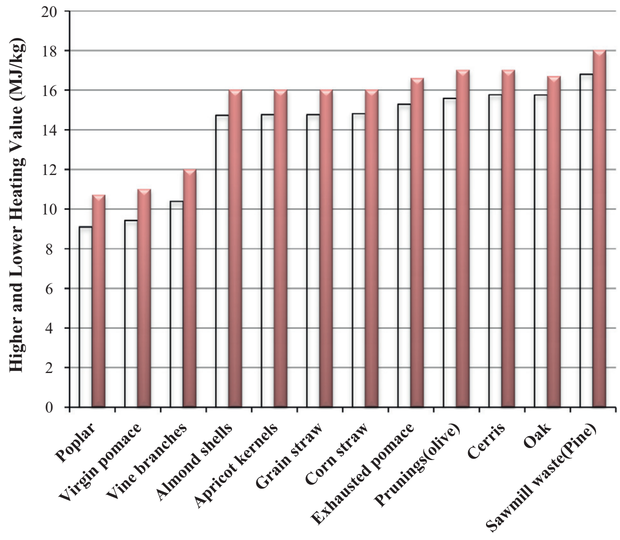

**Fig. 1.** Biomasses evaluated in this work. HHV full histogram and LHV for empty histogram.

### 3.4. Analytical results for cellulose, hemicellulose and lignin

Characterizations is carried out on the matrices it is seen that the proportions between structural components and the extractives are very different between them, although there are some groups of biomass having structural characteristics very similar to each other, thus making it interesting study about the possibility to use mix of different biomass for energy uses.

Below are shown the results of these characterizations:

Fig. 2 shows that the relative percentage of the structural components and of extractives is not unique, however it is possible to identify macro-groups characterized by similar compositions in term of structural components, in agreement with the literature [3].

Component are showed below:

*Group I: Cell > Hemi > Lignin*

The biomass having a cellulose content higher than both hemicellulose and of lignin belong to the firs group. Descending order in cellulose content, belong to the following group the sawmill scraps, Poplar, Oak, Corn Straw and wheat Straw with a relative content of the components showed in Fig. 3:

Group I is composed of 5 species of investigation, with a cellulose content of between 40% by weight for corn straw up to 48% for the sawmill waste. It seems evident that the biomasses related to the group I have an higher content of cellulose respect to the hemicellulose and lignin.

This group is the most representative for the biomass analyzed in this work according to literature analysis [2]. This group is composed both of hard biomass such as poplar and oak [4] but also different straws [5–8], in particular those of wheat [6–10,5,11–13] and corn [9,10,14] according to several literature data.

Cerris falls within the group I, both in terms of structural composition although lignin content is higher than the hemicellulose, although this value depending to the growth area [15].

Fig. 4 shows the structural composition of cerris and almond shells. For the Cerris is possible to note that ligninic content is similar to that Hemicellulosic but significantly lower than the cellulosic, similar to other types of woody biomass of the group I, conversely, for the almonds shells from literature data is present into the group I [16] although the experimental results of analysis show a fair distribution between the 3 components, cellulose, hemicellulose and ligninic.

*Group II: Hemi > Lignin > Cell*

The group II is representative of biomasses characterized by an higher hemicellulosic and ligninic content than to the cellulosic. To this group belong essentially biomass such as bark, foliage, branches [10,17]. These biomasses are not structured and consequently with low mechanical resistance.

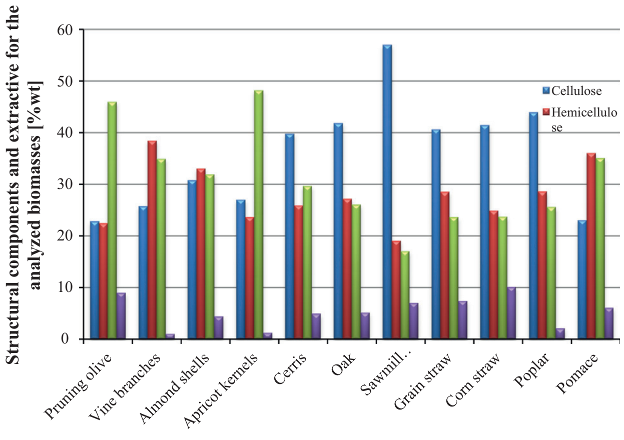

**Fig. 2.** Structural components and extractive for the analyzed biomasses.

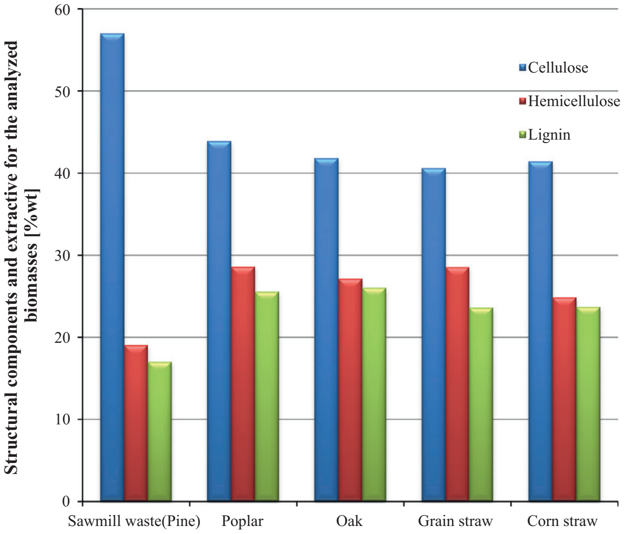

**Fig. 3.** Structural components and extractives of the Group I.

Among the biomass investigation belong to that group there are vine branches with a distribution between the structural components as shown below:

Fig. 5 shows the cellulosic content of biomass related to the group II that is approximately 20% lower than the biomass of the group I while hemicellulose and lignin contents are greater 10% wt than group I

*Group III: Lignin > Cell ~ Hem*

Group III is characteristic for biomass with a ligninic content higher than cellulose and hemicellulose. In this group there are biomass with an high lignin content typical of nuts and pruning olive [10,12,18].

Fig. 6 shows the biochemical composition of the analyzed biomasses that falling within the group III:

The low content of both cellulosic and hemicellulosic species in the Group III and the high ligninic content does not allow their use for the production of bioethanol by hydrolysis or steam explosion, although the higher calorific value of hemicellulose and lignin compared to cellulose is a good starting point for a valuation of these types of biomass for the power production and heat through thermochemical processes.

### 3.5. Organic non-structural components: extractives

Extractives are not structural components of biomass that include simple sugars, fats, waxes, gums, pectins, terpenes, resins, fatty acids, etc. Their calorific value is extremely high, about twice as the cellulose and hemicellulose, and their greater presence (along with lignin) in the conifers explains the higher calorific value than the biomass from hardwoods.

The following table shows the experimental results regarding the extractive content into the biomass for each of the analyzed species (see Fig. 7).

Figure 7 show the obtained results show that the herbaceous biomasses, in particular straw, have a significantly higher content of extractives respect to woody biomass and this result is in line with results obtained from the literature [4,19].

Extractives content decreases with decreasing of the rotation period of the growing [20], also decreases as the diameter of the

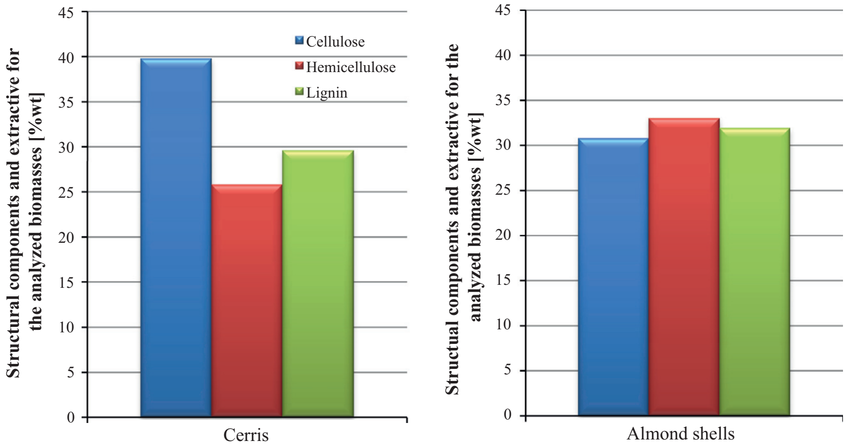

**Fig. 4.** Structural components and extractives for Cerris and Almond shells.

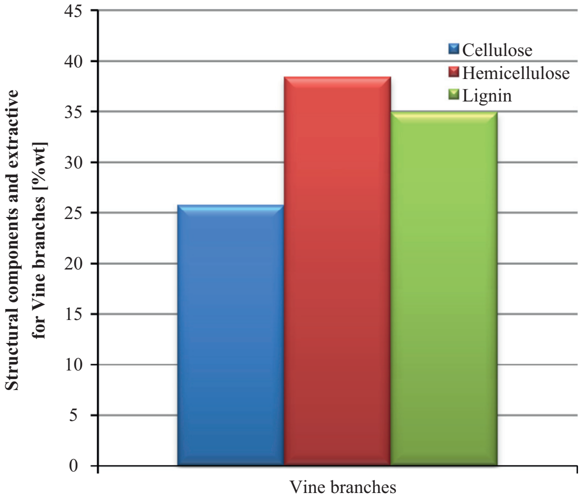

**Fig. 5.** Structural components and extractives that belong at Group II.

biomass [8]. In some cases, such as soybeans, its content is significantly higher compared to other types of biomass [21]. Analysis of the literature also show a positive correlation between the content of extractives with that of silica, while this effect is reversed with the carbon, manganese and magnesium [3].

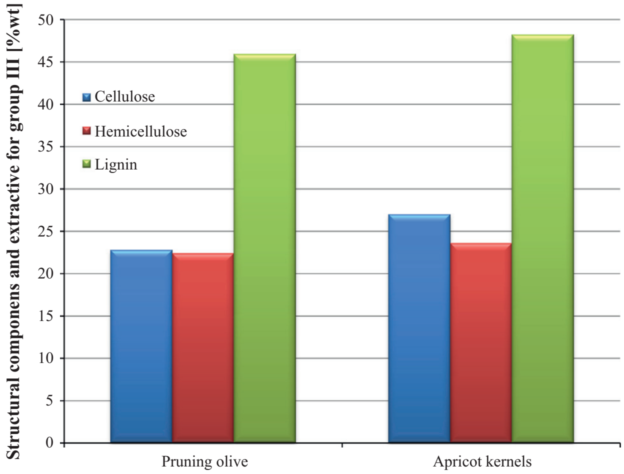

**Fig. 6.** Structural components and extractives that belong at Group III.

The experimental results regarding the biochemical composition of the biomass selected has allowed of grouping into 3 main families of matrices. Into group I there are biomasses with a greater content of cellulose than hemicellulose and lignin. In this group there are wood biomass such as hardwood, conversely, group II is characterized by an higher content of hemicellulose belong soft biomasses such as bark, foliage, pruning of branches and in many case biomasses not structured and biomasses with low mechanical resistance. Last class is the group III composed by biomasses with a high lignin content, typical of part of the kernels and shells.

Ultimately, this grouping allows to determine the biochemical similarities of biomass in order to group matrices that could potentially be used as energy mix with similar structural and chemical features, although it is necessary to take into account other factors which may be discriminatory in final selection of the feasibility for their mixing [22].

### 3.6. Proximate analysis

#### 3.6.1. Ash content

Determination of the ashes content was made with reference to the methods indicated, in particular incineration has been realized in a muffle furnace at 550 ± 10 °C on the sample dried at 105 °C in porcelain crucibles.

The heating of the samples was carried out according to the following scheme:

- first heating up to 250 °C at 5 °C/min for about 60 min;
- raising the temperature up to 550 °C for 120 min.

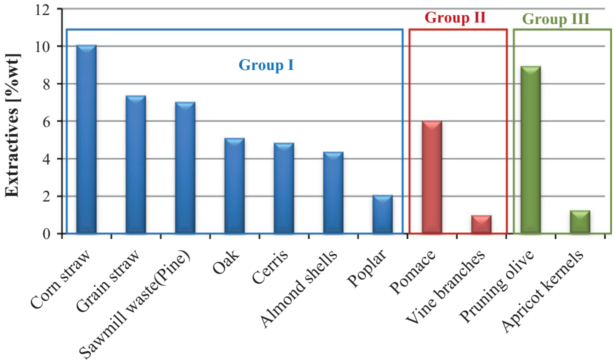

**Fig. 7.** Extractive content in the biomasses.

All weighings were performed after thermally stabilized in a desiccator:

Fig. 8 shows the ash content for each biomasses investigated. It can be seen that sawmill waste and prunings have an ash content below 1% by weight, conversely for the straws there are values of about 10%.

The possibility of transforming the residual biomass for power production is linked both to the type and a the availability of the raw materials.

The residual biomass deriving from scraps of pruning are the most suitable to the heat treatment for both the low ash content and for the possibility of finding significant amounts in the regional context, while, others biomasses such as straws have many problems in term of availables, significantly lower than the residues from pruning. This is certainly a secondary problem, in fact, thermally treating of straws it is possible to produce an high quantities of ash that contain silica that abrade the mechanical parts of the plants and causing problems in their management.

For these reasons is very difficult to treat straws in thermal processes while it is much more convenient the thermal treatment of lignocellulosic biomasses.

### 3.7. Volatiles matter and fixed carbon

Volatile matter represents the fraction that can be extracted under weak heating in absence of air. The reactivity of the volatiles matter is clearly greater than solid matrix, the amount of volatile matter and their speed production are important factors for the selection and sizing of power plants for biomass conversion for energy purposes.

The volatile substance is determined as the weight loss of the sample less of its moisture after heating under standard conditions in the absence of air.

The analytical method used for the determination of the volatile substance is referred to the standards EN 15148 and ASTM 3175. The volatile substance is determined by the weight loss resulting from the heating of the sample, dried at 105 °C, and after increasing the temperature up to 900 ° ± 10 °C for 7 min in a muffle. The solid residue resulting, net of ash, represents the fixed carbon.

The figure below shows are the average data values of five experimental measurements with repeatability allowed less than 3%.

The fraction that still remains after keeping the biomass at high temperature for several minutes is composed by ashes and fixed carbon. Figs. 9 and 10 show that the fixed carbon content is in the range 14–20% by weight and 80–85% by weight of volatile matter.

### 3.8. Ultimate analysis

Ultimate analysis was performed in addition to the determination of the elements: C, H and O were also determined the elements N, S and Cl whose high concentrations may cause emission problems.

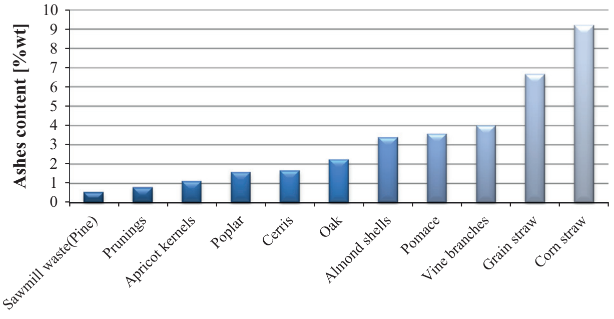

**Fig. 8.** Ashes content in the analyzed biomasses.

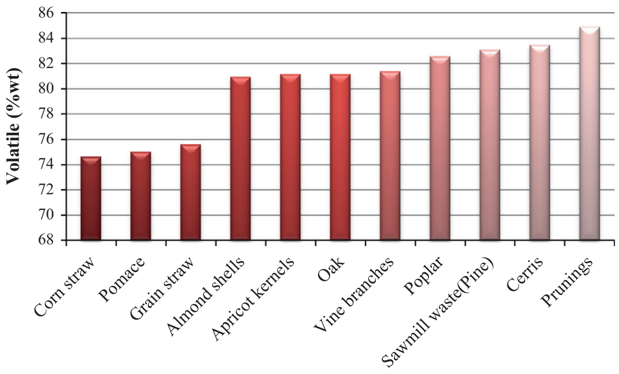

**Fig. 9.** Volatile matter content in the analyzed biomasses.

The reference standard used for the determination of carbon, hydrogen and nitrogen is the CEN/TS 15104. The instrumental apparatus used in the laboratory for this determination is the elemental analyzer CHNS/O 2400 Perkin Elmer.

The principle is based on the complete combustion of a known amount of sample contained in capsules of pure tin in oxygen and with vanadium and tungsten catalysts and subsequent catalyzed reduction of the nitrogen oxides, the homogenization and detection of the combustion products with a thermal conductivity detector.

The main standards used for the instrument calibration are:

| | | |
|---|---|---|
| Acetanilide | $C_8H_9NO$ | C% 71.1; H% 6.7; N% 10.4 |
| Benzoic acid | $C_7H_6O_2$ | C% 68.8; H% 5.0; N% 0 |
| Cystine | $C_6H_{12}N_2O_4S_2$ | C% 30.0; H% 5.0; N% 11.7 |
| Sulphanil Amide | $C_6H_8N_2O_2S$ | C% 41.8;H% 4.7;N% 16.3 |

Fig. 11 shows that is possible to see that as far as the elemental analysis of biomasses were found several similarities in terms of:

- composition by weight of carbon and oxygen in the range 40–50 wt%;
- hydrogen content of about 5–6 wt%;
- nitrogen less than 1%, except for the vine branches that is about 3%.

### 3.9. Sulfur and chlorine content

Combustion is carried out in a calorimetric bomb at the end to ensure the reaction products recovery and after exhaust gases were let bubble in alkaline solution.

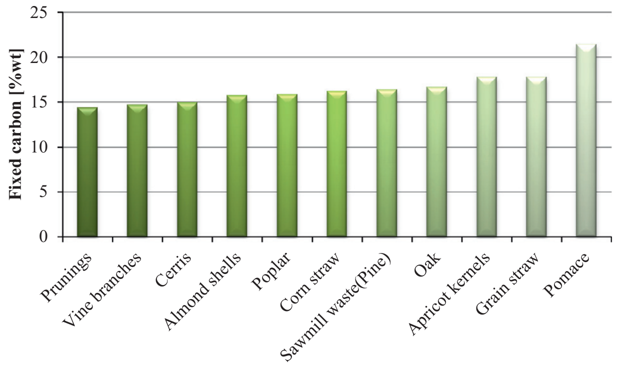

**Fig. 10.** Fixed Carbon in the analyzed biomasses.

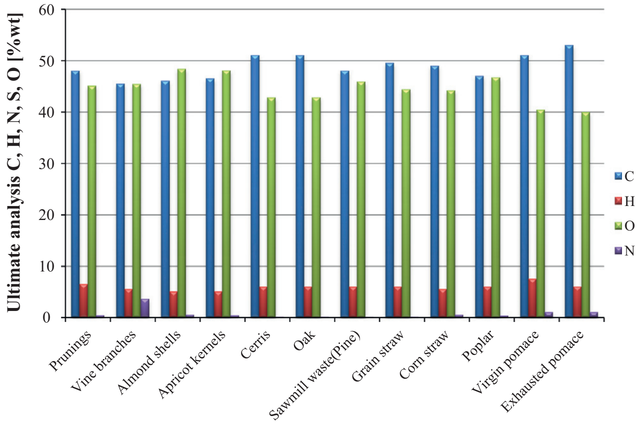

**Fig. 11.** Ultimate analysis CHNO for analyzed biomasses.

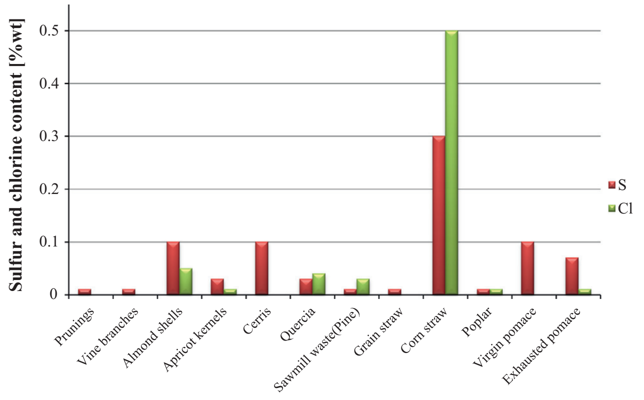

**Fig. 12.** Sulphur and Chlorine content for analyzed biomasses.

In this solution, Cl and S elements are anions such as chloride and sulfate and can be quantified by ion chromatography Dionex (see Fig. 12).

Gasification processes produce hydrogen sulfide, hydrochloric acid in predominant measure, as well as in COS carbonyl sulfide and other secondary compounds containing Cl and S in fact in the biomasses there's an high sulphur and chlorine content as is possible to see in fig. 12. These compounds cause corrosion in the pipeline of plants as well as in the engines and therefore is necessary a cleaning section in order to restrict their concentrations and preserve the devices used for the syngas conversion.

### 3.10. Thermal behavior of the ashes

Determination of macro and micro elements content in the ashes are carried out in order to predict the thermal behavior of the same. The standard used was CEN/TS 15290 for determination of Na, Mg, Ca, K, Fe, Al, Si and P.

The method is based on the acid digestion in a Teflon pressurized vessel at controlled temperature and measuring the elements in the solution. The analytical technique used in our laboratory for the quantitative determination of the elements of interest is the Inductively Coupled Plasma Optical, the laboratory is equipped with a Varian 720 ICP–OES.

The procedure is used for both direct determination on the biocombustile and on the ashes.

The solubilization has Been Realized in closed containers of Teflon in microwave. The sample was first treated in open vessels with hydrogen peroxide and after by additions of both nitric acid and hydrofluoric acid and heating up to 220 °C for about 180 min. After cooling the excess of hydrofluoric acid was neutralized with boric acid and the sample was again heating for 30 min.

The resulting solution was analyzed using the ICP analytical methods optimized for the elements of interest. Fig. 13 shows the results of ashes mineralization:

As can be seen in Fig. 13, alkali metals contained in the ashes are comparable to the silica; these components react at temperatures of about 900 °C producing alkaline silicates that have melting points below 700 °C causing sintering phenomena. This phenomenon can also cause both corrosion and deposition in the devices of syngas conversion. This phenomenon is marked for the straws where the silica percentage in the ashes is very high according to several literature data [23].

Several research centers have proposed studies at the end to evaluate the effect of the ash type in order to obtain a prediction of the thermal behaviors of the same. In particular, the two most important parameters are the alkaline index (AI) and the acid–base ratio in the ash from biomass [24,25]. They are defined as:

$$AI = kg(K_2O + Na_2O)/HHV \qquad (4)$$

### 3.11. AI alcaline index

Values of alkaline index in the range of 0.17–0.34 kg/GJ make it probable foulig and slagging problems, while for AI greater 0.34 these phenomena will certainly be presents in the reactor

$$R_{a/b} = \frac{\%(Fe_2O_3 + CaO + MgO + K_2O + Na_2O)}{\%(SiO_2 + TiO_2 + Al_2O_3)} \qquad (5)$$

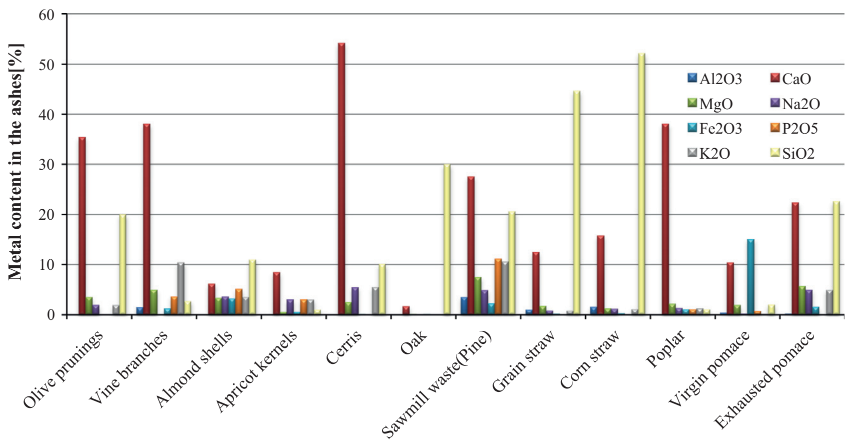

**Fig. 13.** Metal content in the ashes.

### 3.12. $R_{a/b}$ acid–base ratio

Trend of $R_{b/a}$ is related to the likelihood of fouling in the ashes. Possible solutions to overcome these phenomena can be the addition of powder additives such as kaolin, talc and feldspar in order to increase them the melting temperature as soon as calcium and magnesium have the same effect [26] while, sodium and potassium, conversely causes a decreased of melting temperature [27].

Determination of trace elements for the solids biomasses used in pyrogasification processes such as Mn, Cd, Cr, Cu, Ni, Zn, Ti, Pb refers to CEN/TS 15297.

Into solid biofuels low concentrations of these elements are normally present, however high concentrations of them may result from contamination of the sample or cultivation of the same in polluted areas highlighted with the accumulation of some elements such as cadmium. Excessive concentrations of heavy metals constitute a problem in the disposal of the same; reference values of the concentrations of the elements in virgin biomass are given in EN 14961.

Analytical method is based on the acid digestion in pressurized vessel at controlled temperature with a detection of these elements by Inductively Coupled Plasma Optical ICP-OES Varian 720S.

Below are showed the results for selected biomasses in term of their content of the 7 main heavy metals that can be present in biomass: Cadmium, Cd, Lead, Pb, Chromium, Cr, Titanium, Ti, Copper, Cu, Zinc, Nickel and Zn, Ni (see Fig. 7).

Analysis of heavy metals in the ashes has identified 7 main species present as is possible to see in fig. 14. Among these, cadmium

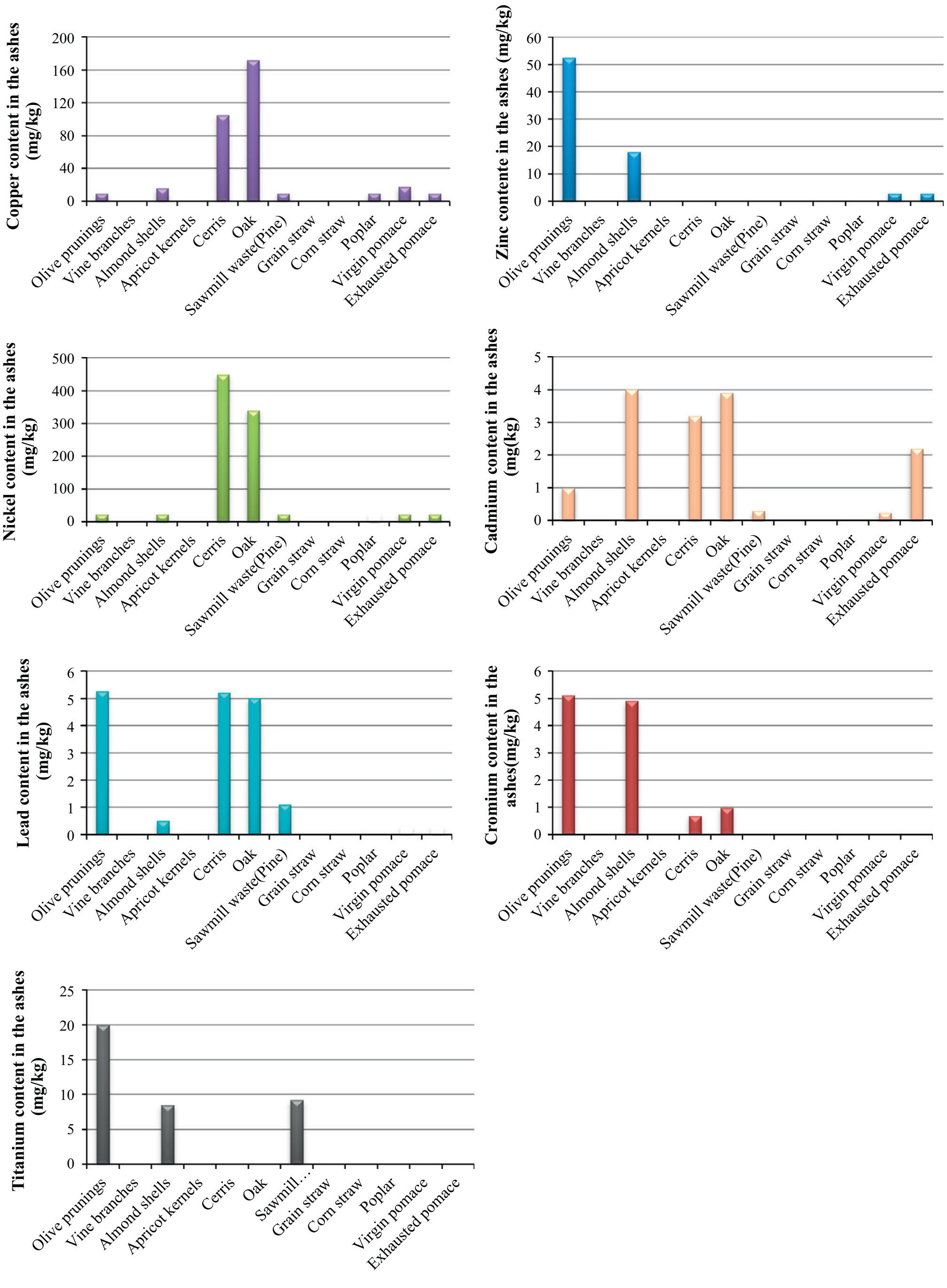

**Fig. 14.** Heavy metal content in the ashes.

is present in different biomasses in the range 0–4 mg/kg, vice versa, the elemental chromium is detectable only in the prunings olive and almond shells with concentrations less than 5.1 mg/kg. Cerris and oak represent those with a greater number of heavy metals and with highest concentration, in particular for these species is high the copper concentration in fact its range is 100–170 mg/kg and this value is similar to the literature datas. Analogously lead content is possible to see concentration of about 270 mg/kg in agreement with literature datas. At the other hand, for the nickel content in the hardwood found in the literature datas are conflicting with each other and with dependence on the territoriality of the species [28,29].

## 4. Conclusions

The understanding of the ashes thermal behavior, properties and their environmental impact in the long term can represent a high risk for the development of a scenario for the power generation, heat and liquid and gaseous biofuels from biomass that need to be evaluated and studied. Using ash as a byproduct of thermochemical processes is limited by the presence of heavy metals and others inorganic compounds formed as a result of the cracking reactions.

The heavy metals concentration range stems from the differences properties of biomasses and therefore there isn't a unique profile of composition for the ashes, in fact the amount of heavy metals depends of several factors such as climate, growth site and age of plant.

The end used for ashes can be of different in order of their composition for example as agricultural fertilizer or additives in building materials.

The presence of alkali metals and/or alkaline earth metals, chlorine, sulfur and silicon affect the reactivity and leaching the inorganic phases.

The ash can be used as a neutralizing agent and calcinante. Experimental results have shown that the heavy metal content is significantly lower in the fly ash than the bottom ash, and therefore, their mixture may be used as a soil improver to maintain the cycle of nutrients in soils.

The use of biomass for energy recovery is a viable alternative at the use of fossil fuels in terms of pollutants emissions, nevertheless its use involves a considerable production of ash in the range 1–10% with significant implications for the management of gasification processes.

The analysis of the thermal behavior of the ash in the process their life cycle is a challenge for the development of near zero emission technologies such as biomass gasification which one cannot ignore in order to ensure the best management of the biomass resource.

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